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*Published in:*
Journal of Chemical Physics

*DOI:*
10.1063/1.432886



*Publication date:*
1976

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Citation: The Journal of Chemical Physics **65**, 3935 (1976); doi: 10.1063/1.432886
View online: https://doi.org/10.1063/1.432886
View Table of Contents: http://aip.scitation.org/toc/jcp/65/10
Published by the American Institute of Physics

# A molecular-statistical theory of the temperature-dependent pitch in cholesteric liquid crystals

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(Received 2 July 1976)

An interaction between chiral molecules is derived in terms of the orientations of their long molecular principal axes. In analogy with Maier–Saupe and Goossens the derivation is based on the electric multipole expansion. The molecules are assumed to behave as if they were cylindrically symmetric, i.e., the system is locally nematic. As an example the chiral molecules are represented by Kuhn models, and the relevant coupling constants are calculated explicitely. An expression for the free energy is obtained in the molecular field approximation. It is shown that, if only the induced dipole–dipole and the dipole–quadrupole dispersion energies are taken into account, a temperature-independent cholesteric pitch is obtained. This result is traced back to the symmetric character of the interaction. In order to explain the experimental situation one has to introduce, in analogy with Keating, an asymmetry producing interaction. The proposed model is discussed and its thermodynamic properties are calculated in the molecular field approximation. It is found that the magnitude of the reciprocal pitch varies nearly linearly with temperature in agreement with experiment. Interpretational difficulties related to the use of the multipole expansion are discussed.

## I. INTRODUCTION

Nematic mesophases of elongated organic molecules are characterized by orientational order of the long molecular axes along a common "director" represented by a unit vector $\mathbf{n}$. In the well-known molecular statistical theory of Maier and Saupe,[1] this tendency for parallel alignment is ascribed to the anisotropic part of the dipole–dipole dispersion interaction between neighboring molecules. In the simplest version of this model a molecule is represented by a linear polarizability (harmonic oscillator) along the direction of its long rotation axis specified by a unit vector $\mathbf{a}$. This is allowed because the molecules in a nematic behave as if they were cylindrically symmetric. The interaction energy between two neighboring molecules $i$ and $j$ for fixed $\mathbf{a}_i$ and $\mathbf{a}_j$, averaged over all positions of $j$ on a sphere of radius $R_{ij}$ with $i$ as center, is then of the simple form $\bar{V}_{ij} = -J(\mathbf{a}_i \cdot \mathbf{a}_j)^2$. In the spirit of the Maier–Saupe interpretation, the coupling constant $J$ contains a factor $R_{ij}^{-6}$. The usual mean field treatment based on this type of pair interaction immediately leads to the Maier–Saupe results.

Here, we are concerned with a molecular statistical treatment of one-component cholesteric mesophases. In such systems the director $\mathbf{n}$ varies as a function of position, $\mathbf{r}$, in the same way as it would in a nematic twisted uniformly about an axis normal to $\mathbf{n}$. With reference to a right-handed Cartesian coordinate system with $\mathbf{n}(0)$ as $z$ axis and the twist axis as $x$ axis, the components of $\mathbf{n}(\mathbf{r})$ can be represented by $n_x = 0$, $n_y = -\sin qx$, $n_z = \cos qx$. The endpoints of the vectors $\mathbf{n}(x, 0, 0)$ form a helix of wave number $q = 2\pi/p$, where $p$ is the pitch; $q > 0$ corresponds to a right-handed and $q < 0$ to a left-handed helix. It is well known that cholesteric liquid crystal structures are formed only when the molecules are chiral (optically active), i.e., different from their mirror image. In fact, this requirement forms the basis of the molecular theory of Goossens[2] and of the continuum theory of de Gennes[3]; the latter pertains to dilute solutions of chiral molecules in a nematic. Goossens' interpretation of the origin of the cholesteric helix forms a logical extension of the idea of Maier and Saupe for nematics in the sense that it carries the multipole expansion in powers of $(1/R_{ij})$ one step further by including the dipole–quadrupole dispersion energy; it is this term that produces the cholesteric twist. Although Goossens has contributed considerably to our understanding of the cholesteric structure, his theory should be extended from a groundstate theory to a statistical theory.

The first purpose of this paper is, therefore, to present a molecular statistical theory of a cholesteric based on the general idea of Goossens. Instead of the planar molecules with four possible orientations of equal statistical weight employed by Goossens, we introduce a modification that allows the molecules to rotate freely about their long principal axes of inertia. This is consistent with the fact that a cholesteric behaves locally like a nematic, i.e., that the molecules behave as if they were cylindrically symmetric. On the basis of this assumption an explicit expression can be derived for the electrostatic interaction between two chiral molecules in terms of the orientation of their long rotation axes $\mathbf{a}_i$ and $\mathbf{a}_j$, and their relative position $\mathbf{R}_{ij}$. This is done in Sec. II. The results are illustrated for a specific molecular model in Sec. III. A molecular field treatment for a cholesteric, analogous to that of Maier–Saupe for nematics, is presented in Sec. IV. In accordance with a proper interpretation of Goossens' ground state theory, our statistical treatment leads to a pitch that is independent of temperature. Quite apart from the strong temperature dependence

  

due to possible presmectic fluctuations, experiments show, however, that for a one-component cholesteric the absolute magnitude of the "intrinsic" pitch decreases with increasing temperature. The second question we wish to raise is, therefore, the following: Is it possible to obtain a temperature-dependent cholesteric pitch by extending the line of thought initiated by Maier–Saupe and Goossens? This question forms the subject of Sec. V. It is shown that inclusion of higher multipole terms, which produce an asymmetry in the intermolecular interaction, leads to a temperature dependence determined by $(\bar{P}_4/\bar{P}_2)^2$, where the $P$'s are Legendre polynominals and the bars indicate thermal averages. The results are related to the explanation offered by Keating[4] in terms of twiston modes with anharmonic restoring forces, set up in analogy with the thermal expansion of a solid. The main difference between our model presented in Sec. V and models for the cholesteric state as proposed by Priest and Lubensky[5] and Wulf[6] lies in the nature of an asymmetry producing interaction.

A discussion of the results is presented in Sec. VI, with particular emphasis on the difficulties encountered by adhering strictly to the electric multipole expansion viewpoint. An alternative suggestion is to consider the intermolecular interaction $V_{ij}$ as an expansion in terms of the angles between $\mathbf{a}_i$, $\mathbf{a}_j$, and $\mathbf{R}_{ij}$ with empirical parameters as coefficients. This is an extension of the viewpoint presented earlier by others in connection with the Maier–Saupe theory.[7]

## II. THE INTERACTION BETWEEN CHIRAL MOLECULES

Our starting point in deriving an explicit expression for the interaction between chiral molecules in a cholesteric liquid crystal, is the electrostatic interaction between the molecules. Considering an arbitrary molecule $i$ to consist of an assembly of point charges $e_{ik}$ situated at $\mathbf{r}_i+\boldsymbol{\rho}_{ik}$, where $\mathbf{r}_i$ denotes the position of the center of mass of the molecule, the electrostatic interaction between two molecules $i$ and $j$ reads

$$H_{ij}=\sum_{k,l}\frac{e_{ik}e_{jl}}{|\mathbf{r}_j-\mathbf{r}_i+\boldsymbol{\rho}_{jl}-\boldsymbol{\rho}_{ik}|}$$

$$=\sum_{k,l}\frac{e_{ik}e_{jl}}{R_{ij}}\left[1+\frac{2}{R_{ij}}\boldsymbol{\rho}_{ij}^{kl}\cdot\mathbf{u}_{ij}+\frac{1}{R_{ij}^2}(\boldsymbol{\rho}_{ij}^{kl})^2\right]^{-1/2}, \qquad (2.1)$$

with

$$R_{ij}=|\mathbf{r}_j-\mathbf{r}_i|\,,\quad \mathbf{u}_{ij}=\frac{\mathbf{r}_j-\mathbf{r}_i}{R_{ij}}\,,\quad \boldsymbol{\rho}_{ij}^{kl}=\boldsymbol{\rho}_{jl}-\boldsymbol{\rho}_{ik}\,.$$

Using the binominal series expansion and rearranging the appearing terms in powers of $R_{ij}^{-1}$ we arrive at the following expansion for the electrostatic interaction:

$$H_{ij}=\sum_{k,l}e_{ik}e_{jl}[R_{ij}^{-1}-R_{ij}^{-2}\boldsymbol{\rho}_{ij}^{kl}\cdot\mathbf{u}_{ij}-R_{ij}^{-3}a_{ij}^{kl}+R_{ij}^{-4}b_{ij}^{kl}+\cdots]\,, \qquad (2.2)$$

where

$$a_{ij}^{kl}=\tfrac{1}{2}[(\boldsymbol{\rho}_{ij}^{kl})^2-3(\boldsymbol{\rho}_{ij}^{kl}\cdot\mathbf{u}_{ij})^2]\,, \qquad (2.2')$$

$$b_{ij}^{kl}=\tfrac{1}{2}[3(\boldsymbol{\rho}_{ij}^{kl})^2-5(\boldsymbol{\rho}_{ij}^{kl}\cdot\mathbf{u}_{ij})^2](\boldsymbol{\rho}_{ij}^{kl}\cdot\mathbf{u}_{ij})\,. \qquad (2.2'')$$

We remark here that the expansion procedure only holds if

$$|2R_{ij}^{-1}\boldsymbol{\rho}_{ij}^{kl}\cdot\mathbf{u}_{ij}+R_{ij}^{-2}(\boldsymbol{\rho}_{ij}^{kl})^2|<1\,. \qquad (2.3)$$

The interaction energy between two chiral molecules $i$ and $j$ is simply obtained by the application of ordinary perturbation theory treating $H_{ij}$ as the perturbation. Neglecting the effect of the possible presence of permanent multipoles we find the first order contribution to be zero. Second order perturbation theory yields the dispersion energy

$$V_{ij}=\sum_{n_i,n_j}{}'\frac{\langle 0_i0_j|H_{ij}|n_in_j\rangle\langle n_in_j|H_{ij}|0_i0_j\rangle}{E_{0_i0_j}-E_{n_in_j}}\,, \qquad (2.4)$$

where $|0_i\rangle$ and $|n_i\rangle$ represent the ground state and excited states of molecule $i$, respectively. Substitution of expression (2.2) into (2.4) and neglect of terms containing $(R_{ij}^{-1})^8$ and higher powers of $R_{ij}^{-1}$ results in

$$V_{ij}=\frac{1}{R_{ij}^6}\sum_{n_i,n_j}{}'\frac{\langle 0_i0_j|a_{ij}|n_in_j\rangle\langle n_in_j|a_{ij}|0_i0_j\rangle}{E_{0_i0_j}-E_{n_in_j}}$$

$$-\frac{1}{R_{ij}^7}\sum_{n_i,n_j}{}'\frac{\langle 0_i0_j|a_{ij}|n_in_j\rangle\langle n_in_j|b_{ij}|0_i0_j\rangle+\text{c.c}}{E_{0_i0_j}-E_{n_in_j}}\,, \qquad (2.5)$$

with $a_{ij}=\sum_{k,l}e_{ik}e_{jl}a_{ij}^{kl}$ and $b_{ij}=\sum_{k,l}e_{ik}e_{jl}b_{ij}^{kl}$.

Next we assume that the rotations of the molecules around their long molecular principal axes are uncorrelated, i.e., the system is locally uniaxial. For that purpose we attach to each molecule $i$ a Cartesian coordinate system with its origin in $\mathbf{r}_i$ and its coordinate axes along the principal axes; then

$$\boldsymbol{\rho}_{ik}=x_{ik}\mathbf{b}_i+y_{ik}\mathbf{c}_i+z_{ik}\mathbf{a}_i\,, \qquad (2.6)$$

where $\mathbf{a}_i$ denotes the unit vector along the long axis ($\mathbf{a}_i$ may be called the "molecular director"), and $\mathbf{b}_i$ and $\mathbf{c}_i$ denote unit vectors along the remaining principal axes. The assumption of uncorrelated rotations around the long molecular axis means that we are allowed to average the expression for the dispersion energy (2.5) over $\mathbf{b}_i$, $\mathbf{c}_i$, $\mathbf{b}_j$, and $\mathbf{c}_j$ under the constraints $\mathbf{b}_i\cdot\mathbf{c}_i=\mathbf{b}_j\cdot\mathbf{c}_j=0$, $\mathbf{b}_i\times\mathbf{c}_i=\mathbf{a}_i$, and $\mathbf{b}_j\times\mathbf{c}_j=\mathbf{a}_j$. The averaging procedure is straightforward, though tedious. During this process we make use of the following two relations (see Appendix) valid for all vectors $\mathbf{n}$ and $\mathbf{m}$, which are not affected by the rotation of molecule $i$, e.g., $\boldsymbol{\rho}_{jl}$ ($j\neq i$) and $\mathbf{u}_{ij}$:

$$(1)\quad \overline{(\mathbf{b}_i\cdot\mathbf{n})(\mathbf{b}_i\circ\mathbf{m})}^{\mathrm{av}}=\overline{(\mathbf{c}_i\cdot\mathbf{n})(\mathbf{c}_i\circ\mathbf{m})}^{\mathrm{av}}$$

$$=\tfrac{1}{2}(\mathbf{n}\cdot\mathbf{m})-\tfrac{1}{2}(\mathbf{n}\cdot\mathbf{a}_i)(\mathbf{m}\cdot\mathbf{a}_i)\,, \qquad (2.7a)$$

$$(2)\quad \overline{(\mathbf{b}_i\circ\mathbf{n})(\mathbf{c}_i\circ\mathbf{m})}^{\mathrm{av}}=\tfrac{1}{2}\mathbf{n}\times\mathbf{m}\circ\mathbf{a}_i\,, \qquad (2.7b)$$

where the average has been taken over $\mathbf{b}_i$ and $\mathbf{c}_i$. The relations (2.7) imply immediately that the dispersion energy will become only a function of $\mathbf{a}_i$, $\mathbf{a}_j$, and $\mathbf{u}_{ij}$. Because of the indistinguishability of the director states $\mathbf{n}$ and $-\mathbf{n}$, i.e., $\mathbf{a}$ and $-\mathbf{a}$ are equally probable, also the terms which are odd in $\mathbf{a}_i$ or $\mathbf{a}_j$ do not contribute. As a result, we obtain the following rather simple expression for the interaction between two molecules $i$ and $j$ in terms of their molecular directors $\mathbf{a}_i$ and $\mathbf{a}_j$:

$$V_{ij} = -J_{ij}^{(1)} - J_{ij}^{(2)}(\mathbf{a}_i \cdot \mathbf{u}_{ij})^2 - J_{ji}^{(2)}(\mathbf{a}_j \cdot \mathbf{u}_{ij})^2 - J_{ij}[(\mathbf{a}_i \cdot \mathbf{a}_j) - 3(\mathbf{a}_i \cdot \mathbf{u}_{ij})(\mathbf{a}_j \cdot \mathbf{u}_{ij})]^2 - K_{ij}[(\mathbf{a}_i \cdot \mathbf{a}_j) - 2(\mathbf{a}_i \cdot \mathbf{u}_{ij})(\mathbf{a}_j \cdot \mathbf{u}_{ij})](\mathbf{a}_i \times \mathbf{a}_j \cdot \mathbf{u}_{ij}) , \tag{2.8}$$

with

$$J_{ij}^{(1)} = \frac{3}{R_{ij}^6} \sum_{n_i, n_j}{}' \frac{[2f_{oni}f_{onj} - f_{oni}\delta_{onj} - f_{onj}\delta_{oni}]}{E_{n_i n_j} - E_{0_i 0_j}} , \tag{2.9a}$$

$$J_{ij}^{(2)} = \frac{9}{R_{ij}^6} \sum_{n_i, n_j}{}' \frac{[f_{onj} - \delta_{onj}]\delta_{oni}}{E_{n_i n_j} - E_{0_i 0_j}} , \tag{2.9b}$$

$$J_{ij} = \frac{9}{R_{ij}^6} \sum_{n_i, n_j}{}' \frac{\delta_{oni}\delta_{onj}}{E_{n_i n_j} - E_{0_i 0_j}} , \tag{2.9c}$$

$$K_{ij} = \frac{3}{R_{ij}^7} \sum_{n_i, n_j}{}' \frac{[\delta_{oni}\sigma_{onj} + \delta_{onj}\sigma_{oni}]}{E_{n_i n_j} - E_{0_i 0_j}} \tag{2.9d}$$

and

$$f_{oni} = \tfrac{1}{3}[|p_{xi}^{on}|^2 + |p_{xi}^{on}|^2 + |p_{yi}^{on}|^2] , \tag{2.10a}$$

$$\delta_{oni} = \tfrac{1}{3}[|p_{zi}^{on}|^2 - \tfrac{1}{2}|p_{xi}^{on}|^2 - \tfrac{1}{2}|p_{yi}^{on}|^2] , \tag{2.10b}$$

$$\sigma_{oni} = \tfrac{3}{2}[p_{xi}^{on} q_{yzi}^{no} - p_{yi}^{on} q_{zxi}^{no}] + \text{c.c.} . \tag{2.10c}$$

The quantities $p_{xi}^{on}$, $p_{yi}^{on}$, $p_{zi}^{on}$, $q_{yzi}^{on}$, and $q_{zxi}^{on}$ are transition probabilities between the groundstate $|0\rangle$ and an excited state $|n\rangle$ of molecule $i$ for the components $p_{\alpha i} = \sum_k e_{ik}\alpha_{ik}$ $(\alpha = x, y, z)$ of the electric dipole moment and for the components $q_{\alpha\beta i} = \sum_k e_{ik}\alpha_{ik}\beta_{ik}$ $(\alpha, \beta = x, y, z)$ of the electric quadrupole moment, e.g.,

$$p_{xi}^{on} = \langle 0_i | \sum_k e_{ik} z_{ik} | n_i \rangle ,$$

$$q_{yzi}^{on} = \langle 0_i | \sum_k e_{ik} y_{ik} z_{ik} | n_i \rangle ,$$

where $\sum_k e_{ik} z_{ik}$ is the component of the electric dipole moment along the long molecular principal axis. We note here that, as was to be expected, $f_{oni}$, $\delta_{oni}$, and $\sigma_{oni}$ are invariant under a coordinate rotation around the $z$ axis; $\delta_{oni}$ is nonzero only if the molecule has an anisotropic polarizability; $\sigma_{oni}$ is zero if the molecule possesses an inversion center or a plane of symmetry perpendicular to the long axis. In contrast with Goossens, we do not get the term $p_{xi}^{on} q_{xyi}^{no}$ in our expression (2.10c) for $\sigma_{oni}$. This term is absent because of our averaging procedure about the long axes. The expression for the dispersion energy (2.8) contains both parallel orienting and rotation terms. The term with coefficient $K_{ij}$ causes the twist in cholesterics, as will be shown.

Summarizing, it can be stated that we can derive a relatively simple expression for the dispersion energy between two molecules under the following assumptions:

(1) The binominal series expansion for the electrostatic interaction is allowed;

(2) Perturbation theory holds;

(3) The molecules rotate uncorrelated around their long molecular principal axes, or behave as if they were cylindrically symmetric.

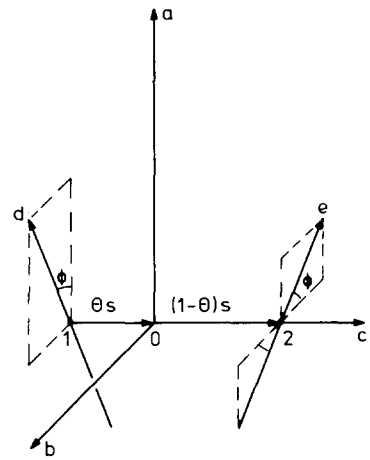


FIG. 1. The Kuhn model, consisting of two linear harmonic oscillators 1 and 2 separated by the distance vector $s\mathbf{c}$ and restricted to oscillate along the unit vectors $\mathbf{d}$ and $\mathbf{e}$, respectively; $\mathbf{d} \perp \mathbf{e}$, $\mathbf{d} \perp \mathbf{c}$, and $\mathbf{e} \perp \mathbf{c}$.

We will return to the validity of these assumptions later.

## III. APPLICATION TO MOLECULAR MODELS

As illustrative examples we treat here the interactions between optically active molecules in terms of simple molecular models. Notably, we pay attention to Kuhn's[8] model of an optically active molecule. The advantage of these models lies in the fact that they provide us with a simple and physically transparent explanation of the appearance of the cholesteric phase; in particular, they show clearly that free rotation around the long molecular axis does not destroy the helical structure.

### A. The Kuhn model

This model consists of two coupled linear harmonic oscillators, which move both perpendicular to each other and to the distance vectors $\mathbf{s} = s\mathbf{c}$ ($\mathbf{c}$ is a unit vector) connecting their centers. The constituents of the oscillator may be considered to be a positive charge $+e$ situated in its center and an oscillating negative charge $-e$. It is clear that the mutual interaction between two Kuhn models is based on electric forces. The motion of the first oscillator is described by the coordinates $\mathbf{x}_1 = x_1\mathbf{d} - \Theta\mathbf{s}$ and that of the second oscillator by the coordinates $\mathbf{x}_2 = x_2\mathbf{e} + (1-\Theta)\mathbf{s}$. The unit vector $\mathbf{d}$ makes an angle $\phi$ with the long molecular axis $\mathbf{a}$, which is perpendicular to $\mathbf{s}$ and divides this vector in two parts, $\Theta\mathbf{s}$ and $(1-\Theta)\mathbf{s}$, $0 \leq \Theta \leq 1$ (see Fig. 1). We take

$$\mathbf{d} = \mathbf{a}\cos\phi + \mathbf{b}\sin\phi , \quad \mathbf{e} = \mathbf{a}\sin\phi - \mathbf{b}\cos\phi , \tag{3.1}$$

where the unit vectors $\mathbf{b}$ and $\mathbf{c}$ may be thought, although not necessarily, to represent the remaining principal axes.

The Hamiltonian of the Kuhn model reads

$$H_k = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_2^2} + \tfrac{1}{2}m\omega_d^2 x_1^2 + \tfrac{1}{2}m\omega_e^2 x_2^2 + k x_1 x_2 , \tag{3.2}$$

where $\omega_d$ and $\omega_e$ denote the frequencies of the $d$- and $e$ oscillator, respectively, while $k$ represents the coupling strength between both oscillators. The Hamiltonian (3.2) can be easily diagonalized by means of the following transformation:

$$y_1 = x_1 \cos\alpha + x_2 \sin\alpha , \qquad y_2 = -x_1 \sin\alpha + x_2 \cos\alpha . \tag{3.3}$$

The result is

$$H_k = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y_1^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial y_2^2} + \tfrac{1}{2} m\omega_1^2 y_1^2 + \tfrac{1}{2} m\omega_2^2 y_2^2 , \tag{3.4}$$

with

$$\omega_1^2 = \tfrac{1}{2}(\omega_d^2 + \omega_e^2) + \tfrac{1}{2}(\omega_d^2 - \omega_e^2)\cos 2\alpha - \frac{k}{m}\sin 2\alpha , \tag{3.5a}$$

$$\omega_2^2 = \tfrac{1}{2}(\omega_d^2 + \omega_e^2) - \tfrac{1}{2}(\omega_d^2 - \omega_e^2)\cos 2\alpha + \frac{k}{m}\sin 2\alpha , \tag{3.5b}$$

$$\alpha = \tfrac{1}{2}\arctan\left(\frac{2k}{m\omega_e^2 - m\omega_d^2}\right) .$$

The eigenvalues and eigenfunctions of harmonic oscillators are well known, i.e., the relevant transition probabilities in (2.10) can be calculated. With some effort we find the following expression for the coupling constants $J_{ij}$ (2.9c) and $K_{ij}$ (2.9d) in the limit $\omega_d \ll \omega_e$ and $\alpha$ small:

$$J_{ij} = \frac{\hbar e^4}{8m^2\omega_1^3 R_{ij}^6}\{P_2[\cos(\alpha - \phi)]\}^2 , \tag{3.6a}$$

$$K_{ij} = \frac{3\hbar e^4 s\Theta}{8m^2\omega_1^3 R_{ij}^7} P_2[\cos(\alpha - \phi)]\sin 2(\alpha - \phi) , \tag{3.6b}$$

where $P_2(z)$ denotes the second Legendre polynominal, $P_2(z) = \frac{3}{2}z^2 - \frac{1}{2}$. (N.B. In the case $\alpha = 0$ and $\omega_e = \infty$, we are left with a molecule without optical activity. However, we still keep the twist as long as $\phi \neq 0$ and $s\Theta \neq 0$ provided that the molecules rotate uncorrelated around their long molecular principal axes.)

### B. The helicoidal model[9]

A second simple model for an optically active molecule is a harmonic oscillator, which is constrained to oscillate along a helicoidal curve with parameter representation $x = x(\xi)$, $y = y(\xi)$, $z = z(\xi)$. Such a model bears a slight resemblance to the shape of a cholesteryl esther. The Hamiltonian of this model reads

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{d\xi^2} + \tfrac{1}{2} m\omega^2\xi^2 . \tag{3.7}$$

It is clear that we will find the coefficient to the twist term to be unequal to zero. The coefficient $K_{ij}$ will depend on the shape of the curve in this case.

## IV. MOLECULAR FIELD APPROXIMATION FOR A ONE-COMPONENT CHOLESTERIC

The interaction (2.8) between chiral molecules in a cholesteric contains two important terms. The first term,

$$-J_{ij}[(\mathbf{a}_i \cdot \mathbf{a}_j) - 3(\mathbf{a}_i \cdot \mathbf{u}_{ij})(\mathbf{a}_j \cdot \mathbf{u}_{ij})]^2 , \tag{4.1a}$$

which is nothing but the Maier–Saupe induced dipole–dipole interaction and is due to the anisotropy of the molecules, gives rise to the nematic state. The second term,

$$-K_{ij}[(\mathbf{a}_i \cdot \mathbf{a}_j) - 2(\mathbf{a}_i \circ \mathbf{u}_{ij})(\mathbf{a}_j \circ \mathbf{u}_{ij})](\mathbf{a}_i \times \mathbf{a}_j \circ \mathbf{u}_{ij}) , \tag{4.1b}$$

which is due to the asymmetry of the molecules, induces a twist into the system resulting in the cholesteric state. In the following we will calculate, within the framework of the molecular field approximation, the thermodynamic stability of the cholesteric phase and the temperature dependence of both the pitch $p$ of the helical structure and the long range order parameter.

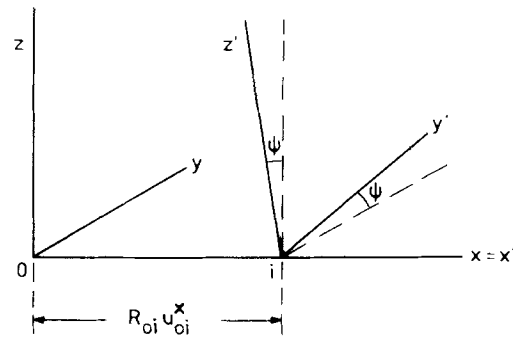


FIG. 2. Local coordinate system $x'$, $y'$, $z'$ along the helical axis; the rotation angle around the $x$ axis is $\psi = qR_{0i}u^x_{0i}$.

Because of the rather short range character of the interaction we only take nearest neighbor interactions into account, i.e., the interaction energy between a given molecule with orientation $\mathbf{a}_0$ and the remaining system reads

$$V_0 = -\sum_{i=1}^{\gamma} J_{0i}[(\mathbf{a}_0 \cdot \mathbf{a}_i) - 3(\mathbf{a}_0 \cdot \mathbf{u}_{0i})(\mathbf{a}_i \cdot \mathbf{u}_{0i})]^2 - \sum_{i=1}^{\gamma} K_{0i}[(\mathbf{a}_0 \cdot \mathbf{a}_i) - 2(\mathbf{a}_0 \cdot \mathbf{u}_{0i})(\mathbf{a}_i \cdot \mathbf{u}_{0i})](\mathbf{a}_0 \times \mathbf{a}_i \cdot \mathbf{u}_{0i}) , \tag{4.2}$$

where the summation index $i$ runs over the number of nearest neighbors, $\gamma$. Basically the molecular field approximation boils down to the following procedure in the present case: we assume the existence of a twisted structure with helical wave number $q = (2\pi/p)$, and subsequently we show that this structure is indeed thermodynamically stable in a certain temperature region. In order to proceed we define a coordinate system $x$, $y$, $z$ with its origin at the center of the molecule with molecular axis $\mathbf{a}_0$ such that the $x$ axis is along the helical axis and the $z$ axis along the average direction of the molecule, i.e., along the local director. As reference system for molecule $i$ located at $\mathbf{R}_{0i}$ we introduce the system $x'$, $y'$, $z'$ such that $x'$ lies again along the helical axis and $z'$ along the local director $\mathbf{n}(\mathbf{R}_{0i})$. This implies that $z'$ and $y'$ can be obtained by rotation over an angle $qR_{0i}u^x_{0i}$ around the helical axis (see Fig. 2). With respect to the $x'$ $y'$ $z'$ system the components of $\mathbf{a}_i$ are given by $a'_{ix}$, $a'_{iy}$, $a'_{iz}$, while they are $a_{ix}$, $a_{iy}$, and $a_{iz}$ with respect to the $x$, $y$, $z$ system. It is easy to see that

$$a_{ix} = a'_{ix} , \tag{4.3a}$$

$$a_{iy} = a'_{iy}\cos(qR_{0i}u^x_{0i}) - a'_{iz}\sin(qR_{0i}u^x_{0i}) , \quad (4.3b)$$

$$a_{iz} = a'_{iy}\sin(qR_{0i}u^x_{0i}) + a'_{iz}\cos(qR_{0i}u^x_{0i}) . \quad (4.3c)$$

Next we make the following three assumptions, which are consistent with the symmetry of the cholesteric phase.

(1) The distributions of the possible orientations of the molecular axis **a** around the local director is uniaxial, i.e., the system is locally nematic. This assumption is justified because $qR < 10^{-2}$, where $R$ denotes the mean intermolecular distance. In terms of spherical coordinates we have with respect to the local coordinate systems

$$a_{0x} = \sin\theta_0\cos\phi_0 , \quad a_{0y} = \sin\theta_0\sin\phi_0 , \quad a_{0z} = \cos\theta_0 , \quad (4.4a)$$

$$a'_{ix} = \sin\theta'_i\cos\phi'_i , \quad a'_{iy} = \sin\theta'_i\sin\phi'_i ,$$

$$a'_{iz} = \cos\theta'_i \quad (i = 1, 2, \ldots, \gamma) . \quad (4.4b)$$

Because of the cylindrical symmetry we are allowed to average over the azimuth angles $\phi_0$ and $\phi'_i$ and we may write

$$\overline{a^2_{0x}} = \overline{a^2_{0y}} = \tfrac{1}{3}[1 - P_2(a_{0z})] , \quad a^2_{0z} = \tfrac{1}{3}[1 + 2P_2(a_{0z})] , \quad (4.5a)$$

$$\overline{a'^2_{ix}} = \overline{a'^2_{iy}} = \tfrac{1}{3}[1 - P_2(a'_{iz})] , \quad a'^2_{iz} = \tfrac{1}{3}[1 + 2P_2(a'_{iz})] , \quad (4.5b)$$

where $P_2(z)$ is the second Legendre polynominal.

(2) In analogy with the theory of Maier and Saupe for nematics, we take the distribution of the nearest neighbors of a given molecule to be spherically symmetric and we neglect the correlation between positions and orientations. This assumption is consistent with the liquid phase and yields reasonable results in the case of nematics. In practice it means that we are allowed to put $R_{0i}$ equal to the mean intermolecular distance $R$ (i.e., we replace $J_{0i}$ by $J$ and $K_{0i}$ by $K$), and to average functions of $\mathbf{u}_{0i}$ over a sphere.

(3) We assume $qR_{0i}u^x_{0i} \ll 1$, which allows a simple expansion of $\sin(qR_{0i}u^x_{0i})$ and $\cos(qR_{0i}u^x_{0i})$.

After carrying out the steps involved in these assumptions we arrive at the following expression for the interaction energy:

$$V_0 = [-J(\tfrac{2}{15} - \tfrac{11}{105}q^2R^2) - \tfrac{1}{5}KqR] \times \sum_{i=1}^{\gamma} P_2(a_{0z})P_2(a'_{iz}) + \text{const.} \quad (4.6)$$

The final step in our molecular field approximation is the replacement of $P_2(a'_{iz})$ by the long range order parameter $\bar{P}_2$, i.e., the molecule with director $\mathbf{a}_0$ interacts with the remaining system through a molecular field $\bar{V}_0$ of the following form:

$$\bar{V}_0 = -\gamma\bar{P}_2[J(\tfrac{2}{15} - \tfrac{11}{105}q^2R^2) + \tfrac{1}{5}KqR]P_2(a_{0z}) , \quad (4.7)$$

where we have omitted the constant term. Self-consistency requires the following equation for $\bar{P}_2$:

$$\bar{P}_2 = \frac{1}{Z}\int_{-1}^{1} da_{0z}P_2(a_{0z})\,e^{-\bar{V}_0/k_BT} , \quad (4.8)$$

with

$$Z = \int_{-1}^{1} da_{0z}\,e^{-\bar{V}_0/k_BT} . \quad (4.9)$$

Note that the isotropic solution $\bar{P}_2 = 0$ always satisfies Eq. (4.8). In case this equation allows for more than one solution at a given temperature, the correct, i.e., thermodynamically stable, solution is obtained by the argument that it should possess the lowest free energy $F$ per molecule, where

$$F = \tfrac{1}{2}\gamma[J(\tfrac{2}{15} - \tfrac{11}{105}q^2R^2) + \tfrac{1}{5}KqR]\bar{P}_2^2 - k_BT\ln Z . \quad (4.10)$$

The helical wave number $q$ is determined by the requirement that the free energy $F(q, T)$ should be minimal with respect to $q$, i.e., $\partial F/\partial q = 0$, or

$$q = \frac{21}{22}\frac{K}{JR} . \quad (4.11)$$

From experiment we know that $|qR| \approx 10^{-2}$, i.e., $|K/J| \ll 1$. This inequality can be easily satisfied if the molecules are only slightly asymmetrical. In fact, Goossens has shown by an order of magnitude estimate that $|K/J| \approx 10^{-2}$. Substitution of (4.11) in (4.8), which is nothing but $(\partial F/\partial\bar{P}_2) = 0$, gives us the dependence of $\bar{P}_2$ on $T$, $J$, and $K$. The resulting equation has exactly the same form as the corresponding one in the Maier–Saupe theory. Because of our third assumption we may neglect the dependence on $K$, i.e., $\bar{P}_2$ is completely determined by the induced dipole–dipole interaction and is nothing but the well-known order parameter as described by the Maier–Saupe theory.

Comparing the theory with experiments we find a striking discrepancy: *the pitch does not depend on temperature.* This means that we have to add other interaction terms in order to describe the temperature dependence of the pitch.

## V. TEMPERATURE DEPENDENCE OF THE INTRINSIC PITCH

Experimentally one generally finds that the helical wave number $q$ of a cholesteric system varies with temperature. For systems exhibiting a cholesteric–smectic phase transition at some temperature $T_{CS}$, presmectic fluctuations which increase the twist rigidity as one approaches $T_{CS}$ from above are responsible for the strong temperature dependence of $q$ near $T_{CS}$. Even in such cases, however, there remains an "intrinsic" $(dq/dT)$ in the temperature region sufficiently far above $T_{CS}$, as shown for example in the study of cholesteryl nonanoate by Pindak, Huang, and Ho.[10] In this section we consider only the approximately linear temperature dependence of the intrinsic pitch and not that resulting from smectic short-range ordering.

The results of the previous section can also be obtained by using a simplified version of (4.1). With some effort it can be shown that an interaction between two molecules $i$ and $j$ of the form

$$V_{ij} = -J(\mathbf{a}_i\cdot\mathbf{a}_j)^2 - K(\mathbf{a}_i\cdot\mathbf{a}_j)(\mathbf{a}_i\times\mathbf{a}_j\cdot\mathbf{u}_{ij}) \quad (5.1)$$

gives rise to essentially the same thermodynamic behavior as found in Sec. IV, provided the same assumptions and the molecular field approximation are used. The insensitivity of the pitch to temperature is now

easily understood. Taking the $z$ direction along $\mathbf{u}_{ij}$ and expressing the molecular axes $\mathbf{a}_i$ and $\mathbf{a}_j$ in terms of polar coordinates we obtain

$$V_{ij} = -J\left[\cos\theta_i\cos\theta_j + \sin\theta_i\sin\theta_j\cos(\phi_j - \phi_i)\right] \times\left[\cos\theta_i\cos\theta_j + \sin\theta_i\sin\theta_j\cos(\phi_j - \phi_i - A)\right], \quad (5.2)$$

with $|A| = |K/J| \ll 1$; i.e., the interaction is symmetric with respect to $(\phi_j - \phi_i) = \frac{1}{2}A$. This implies immediately that the helical wave number

$$q = \frac{A}{2R} = \frac{K}{2RJ} \quad (5.3)$$

does not depend on temperature (the slight dependence of $R$ on $T$ can be neglected).

In order to avoid unnecessary mathematical complications we adopt from now on the interaction (5.1) as our starting point for a theory of the cholesteric state. As has already been said, this model gives rise to a cholesteric state with a temperature independent pitch. Clearly, the description of a cholesteric with a temperature dependent pitch requires the addition of new terms to the interaction (5.1). The nature of these terms is obvious; they have to introduce asymmetry into the interaction between the molecules. The relevance of an asymmetrical interaction follows already from Keating's twiston model for the explanation of the temperature dependence of the pitch.

There are, of course, a countless number of ways to add symmetry-breaking terms. We propose to add terms proportional to $(\mathbf{a}_i \circ \mathbf{a}_j)^4$ and $(\mathbf{a}_i \cdot \mathbf{a}_j)^3(\mathbf{a}_i \times \mathbf{a}_j \circ \mathbf{u}_{ij})$ on the basis of the following reasons:

(1) The terms should be invariant with respect to the replacement of $\mathbf{a}_i$ by $-\mathbf{a}_i$, or $\mathbf{a}_j$ by $-\mathbf{a}_j$, or both. Note that the "nematogenic" as well as the "cholesteric" interaction on the right-hand side of (5.1) satisfy this requirement.

(2) On the basis of (1), further nematogenic terms to be added to (5.1) are restricted to those of the form $(\mathbf{a}_i \cdot \mathbf{a}_j)^{2n}$, with $n$ = integer; this justifies addition of a term $(\mathbf{a}_i \cdot \mathbf{a}_j)^4$.

(3) Note that the cholesteric term on the right-hand side of (5.1) has the following properties for given $\mathbf{a}_i$ and $\mathbf{a}_j$: Suppose the position of $\mathbf{a}_i$ is fixed and that of $\mathbf{a}_j$ is variable over a sphere with $i$ as center; the cholesteric term then vanishes for $\mathbf{u}_{ij} \parallel \mathbf{a}_i$, and its magnitude reaches a maximum value for $\mathbf{u}_{ij} \perp \mathbf{a}_i$. In fact, the magnitude of this term varies as the sine of the angle between $\mathbf{u}_{ij}$ and $\mathbf{a}_i$. Since this variation is consistent with the cholesteric structure, as well as with the rotation vector introduced by de Gennes for the nematic director around a chiral molecule in a nematic matrix, we require the same variation of further twist terms. This implies that new twist terms are restricted to those containing $(\mathbf{a}_i \times \mathbf{a}_j) \cdot \mathbf{u}_{ij}$ to the first power. This justifies addition of a term $(\mathbf{a}_i \cdot \mathbf{a}_j)^3\{(\mathbf{a}_i \times \mathbf{a}_j) \circ \mathbf{u}_{ij}\}$.

As a result we obtain a model for a cholesteric based on the following interaction between molecules $i$ and $j$:

$$W_{ij} = -J_{ij}(\mathbf{a}_i \cdot \mathbf{a}_j)^2 - K_{ij}(\mathbf{a}_i \cdot \mathbf{a}_j)\{(\mathbf{a}_i \times \mathbf{a}_j) \circ \mathbf{u}_{ij}\} - L_{ij}(\mathbf{a}_i \circ \mathbf{a}_j)^4 + M_{ij}(\mathbf{a}_i \cdot \mathbf{a}_j)^3\{(\mathbf{a}_i \times \mathbf{a}_j) \cdot \mathbf{u}_{ij}\}, \quad (5.4)$$

where the parameters $J_{ij}$, $K_{ij}$, $L_{ij}$, and $M_{ij}$ are functions of $R_{ij}$. It should be remarked that if the electric multipole expansion is carried to higher order, terms appear which after appropriate averaging yield terms equivalent to the ones proposed here. Also, on the basis of the procedure outlined above terms of order $R_{ij}^{-8}$ and $R_{ij}^{-9}$ must be dropped; $L_{ij}$ and $M_{ij}$ correspond respectively to terms of order $R_{ij}^{-10}$ and $R_{ij}^{-11}$.

We solve this model in the molecular field approximation. As an intermediate step we obtain, after application of the three assumptions mentioned in the previous section, the following interaction energy between a molecule with molecular director $\mathbf{a}_0$ and its nearest neighbors:

$$W_0 = \left[-\tfrac{1}{3}J(2 - q^2R^2) - \tfrac{1}{3}KqR - \tfrac{2}{7}L(2 - q^2R^2) + \tfrac{1}{7}MqR\right] \times\sum_{i=1}^{\gamma} P_2(a_{0z})P_2(a'_{iz}) + \left[-\tfrac{6}{21}L\left(\tfrac{3}{5} - q^2R^2\right) + \tfrac{4}{21}MqR\right] \times\sum_{i=1}^{\gamma} P_4(a_{0z})P_4(a'_{iz}) + \text{const}, \quad (5.5)$$

with $P_4(z)$ denoting the fourth Legendre polynominal, $P_4(z) = \frac{35}{8}z^4 - \frac{30}{8}z^2 + \frac{3}{8}$. Its appearance is due to the averaging process over the azimuth angles, e.g.,

$$\overline{a_{0x}^4} = \overline{a_{0y}^4} = \overline{3a_{0x}^2 a_{0y}^2} = \tfrac{1}{35}P_4(a_{0z}) - \tfrac{2}{21}P_2(a_{0z}) + \tfrac{41}{140},$$

$$\overline{a_{0x}^2 a_{0z}^2} = \overline{a_{0y}^2 a_{0z}^2} = -\tfrac{4}{35}P_4(a_{0z}) + \tfrac{1}{21}P_2(a_{0z}) + \tfrac{4}{15},$$

$$\overline{a_{0z}^4} = \tfrac{8}{35}P_4(a_{0z}) + \tfrac{4}{7}P_2(a_{0z}) - \tfrac{1}{5}.$$

Finally we replace $P_2(a'_{iz})$ and $P_4(a'_{iz})$ by the long range order parameters $\bar{P}_2$ and $\bar{P}_4$. Then the molecule with director $\mathbf{a}_0$ interacts with the system via a molecular field of the form

$$\bar{W}_0 = -\gamma\bar{P}_2\left[\tfrac{1}{3}J(2 - q^2R^2) + \tfrac{1}{3}KqR + \tfrac{2}{7}L(2 - q^2R^2) - \tfrac{1}{7}MqR\right] \times P_2(a_{0z}) + \gamma\bar{P}_4\left[-\tfrac{6}{21}L\left(\tfrac{3}{5} - q^2R^2\right) + \tfrac{4}{21}MqR\right]P_4(a_{0z}), \quad (5.6)$$

where we have omitted the constant term. The order parameters $\bar{P}_2$ and $\bar{P}_4$ are determined self-consistently:

$$\bar{P}_2 = \frac{1}{Z}\int_{-1}^{+1} da_{0z}P_2(a_{0z})\,e^{-\bar{W}_0/k_BT}, \quad (5.7a)$$

$$\bar{P}_4 = \frac{1}{Z}\int_{-1}^{+1} da_{0z}P_4(a_{0z})\,e^{-\bar{W}_0/k_BT}, \quad (5.7b)$$

$$Z = \int_{-1}^{+1} da_{0z}\,e^{-\bar{W}_0/k_BT}. \quad (5.7c)$$

The isotropic solution $\bar{P}_2 = \bar{P}_4 = 0$ always satisfies Eq. (5.7). In case more solutions of this set of equations exist, the thermodynamically relevant one has the lowest free energy per molecule

$$F = \left[\left(\tfrac{1}{3}\gamma J + \tfrac{2}{7}\gamma L\right)\bar{P}_2^2 + \tfrac{4}{35}\gamma L\bar{P}_4^2\right] + qR\left[\left(\tfrac{1}{6}\gamma K - \tfrac{1}{14}\gamma M\right)\bar{P}_2^2 - \tfrac{2}{21}\gamma M\bar{P}_4^2\right] - q^2R^2\left[\left(\tfrac{1}{6}\gamma J + \tfrac{1}{7}\gamma L\right)\bar{P}_2^2 + \tfrac{4}{21}\gamma L\bar{P}_4^2\right] - k_BT\ln Z. \quad (5.8)$$

The helical wave number $q$ is determined by the requirement that the free energy should be minimal with

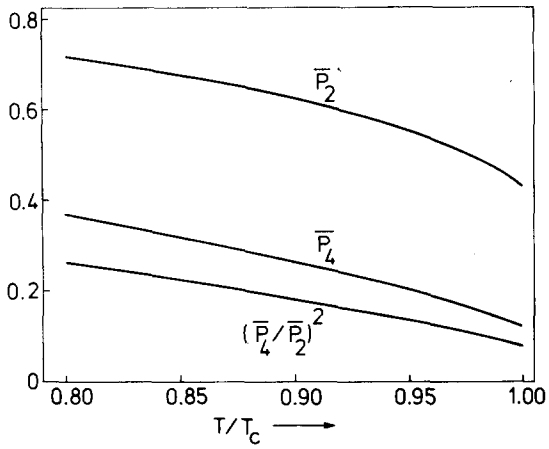


FIG. 3. Temperature dependence of the Maier–Saupe order parameter $\bar{P}_2$, $\bar{P}_4$, and $x^2=(\bar{P}_4/\bar{P}_2)^2$ calculated for the case $K=L=M=0$.

respect to $q$. We obtain

$$q=\frac{1}{R}\left[\frac{(7K-3M)-4Mx^2}{(14J+12L)+16Lx^2}\right] \tag{5.9}$$

with $x=\bar{P}_4/\bar{P}_2$, i.e., *the temperature dependence of the helical wave number $q$ is determined by the ratio of the order parameters $\bar{P}_4$ and $\bar{P}_2$.* Strictly speaking, $\bar{P}_2$ and $\bar{P}_4$ depend on $q$, i.e., (5.9) is an implicit equation for $q(T)$. In practice, however, $qR \ll 1$ so that the $q$ dependence of $\bar{P}_2$ and $\bar{P}_4$, and thus of $x$, can be neglected. Figure 3 shows the temperature dependence of $\bar{P}_2$, $\bar{P}_4$, and $x^2$ calculated for the Maier–Saupe theory. Note that $x^2$ varies roughly linearly with temperature; an order of magnitude estimate yields

$$\frac{d}{dT}\left\{\frac{\bar{P}_4}{\bar{P}_2}\right\}^2 \approx -\frac{1}{T_c}. \tag{5.10}$$

## VI. DISCUSSION

The treatment presented in Sec. II for the interaction between two chiral molecules is similar to that of Goossens in the sense that the interaction is assumed to be electrostatic and that within the multipole expansion scheme only the dipole–dipole and dipole–quadrupole dispersion terms are retained. An essential difference is that we allow free rotation of the molecules around their long principal axes, whereas Goossens considered planar molecules with four distinct orientations of equal statistical weight. Furthermore, we have chosen a binominal series expansion which through (2.3) clearly specifies the conditions required for the validity of the multipole expansion procedure. Our result (2.8) shows that the cylindrically symmetric behavior of the molecules does not destroy the tendency for "cholesteric alignment" described by the competing terms involving $J$ and $K$, contrary to remarks in this connection in Goossens' article.

The result (4.12) obtained from our molecular field approximation in Sec. IV shows that if one only retains the terms with $J$ and $K$, a temperature-independent cholesteric wave number is obtained. Apart from a different numerical factor, arising from our averaging procedure, the result (4.12) is essentially the same as that obtained by Goossens' nonstatistical treatment; the latter corresponds to our formula (5.3). The explanation of the temperature independence of $q$ in this scheme lies in the fact that the potential energy between two molecules is a symmetric function of $(\phi_j-\phi_i-qR)$, where $q$ is given by (5.3).

In order to obtain a temperature-dependent $q$ it is obviously necessary to include higher order terms in the expansion which produce asymmetry in the potential energy as a function of $(\phi_j-\phi_i-qR)$. This has been done in Sec. V and leads to the result (5.9). In this expression there appear, besides $J$ and $K$, two more parameters $L$ and $M$ in combination with the temperature dependent factor $x^2=(\bar{P}_4/\bar{P}_2)^2$. It is of interest to estimate the order of magnitude of $L$ and $M$ required for the description of the temperature dependence of $q$ as observed in cholesterics in a temperature range not too close to a cholesteric–smectic transition. For experimental data for a number of cholesteryl esters we refer to Demus and Wartenberg.[11] As a typical example we consider the data for cholesteryl propionate for which one finds in the temperature range between 78 °C and 110 °C $(dq/dT)\simeq 500\ \mathrm{cm^{-1}\cdot deg^{-1}}$ and $(1/q)(dq/dT)\simeq 0.002\ \mathrm{deg^{-1}}$. Comparison of the latter result with the same quantity obtained from (5.9) and (5.10) with $x^2\approx 0.1$ yields the following order of magnitude relation:

$$\frac{T_c}{q}\frac{dq}{dT}\simeq\frac{4M}{7K-3.4M}+\frac{16L}{14J+13.6L}\approx 1. \tag{6.1}$$

We conclude that this requires $M\approx K$ and/or $L\approx J$. In this connection it should be realized that $L$ is the coefficient of the nematogenic interaction $(a_i\cdot a_j)^4$ and that, consequently, $(L/J)$ influences the Maier–Saupe order parameter; this has been investigated by Humphries, James, and Luckhurst.[12] For example, for $L/J=0$ one obtains the ordinary Maier–Saupe result $\bar{P}_2(T_c)=0.43$, whereas for $L/J=0.5$ one would obtain $\bar{P}_2(T_c)=0.48$. A determination of $L/J$ would thus require reliable measurements of the nematic order parameter. If one were satisfied in this respect with the Maier–Saupe result, one might take $L/J=0$ and ascribe the temperature dependence of the cholesteric wave number completely to the parameter $M$. At any rate, our results indicate a serious difficulty for the electric multipole expansion philosophy because in this approach $J$, $K$, $L$, and $M$ corresponds, respectively, to terms of order $R^{-6}$, $R^{-7}$, $R^{-10}$, and $R^{-11}$. In a properly converging series $L\approx J$ and $M\approx K$ would simply not be acceptable. This takes us to the following more general discussion.

In the preceding sections we adhered as much as possible to the notion that the intermolecular interaction in nematics and cholesterics can be discussed in terms of an electric multipole expansion in powers of $R_{ij}^{-1}$. This has been done intentionally to conform with the line of thought followed by Maier–Saupe and Goossens. Our purpose was, in fact, to present a statistical version of Goossens' theory and to investigate the possibility of obtaining a proper temperature dependence of the cholesteric pitch by extending his line of argument. There

are at least two general arguments, however, that cast doubt on the validity of the multipole expansion viewpoint:

(1) The systems under consideration consist of elongated molecules with dimensions comparable with or even larger than the mean separation $R_{ij}$ between the centers of mass of nearest neighbors. This implies that the condition (2.3) required for proper convergence of the multipole expansion can hardly be satisfied and that the identification of specific multipole interactions with the various terms in the expansion becomes doubtful.

(2) Apart from (1), one might expect important contributions to the anisotropic part of the intermolecular interaction between neighboring molecules from the specific shape of the molecules through repulsive forces (excluded volume effects). Various authors,[7] therefore, have suggested earlier that the Maier–Saupe theory for nematics should be viewed as a phenomenological model and that the intermolecular nematogenic interaction parameter, denoted by $J$ in the preceding sections, should be regarded as containing contributions from both attractive (dipole–dipole dispersion) and repulsive forces. In this connection it should be admitted that de Jeu and Van der Veen[13] have established systematic trends between clearing points and the anisotropy of the polarizability of homologous series of compounds in agreement with the Maier–Saupe theory. More recently, Van der Veen[14] studied the influence of terminal substituents on the clearing temperature which also confirm the importance of the anisotropy of the polarizability. We believe, however, that these results do not invalidate the argument for a "mixed viewpoint."

On the basis of these arguments and our own findings that $M \approx K$ and/or $L \approx J$ in order to obtain a proper description of the temperature dependence of $q$ we are inclined to consider $J$, $K$, $L$, and $M$ introduced in the preceding sections as phenomenological parameters in an expansion of $V_{ij}$ in terms of the angles between $\mathbf{a}_i$, $\mathbf{a}_j$, and $\mathbf{u}_{ij}$, rather than as specific multipole interaction parameters. This viewpoint is similar to that of Humphries, James, and Luckhurst. Further support for this notion may be derived from the following argument:

(3) Stegemeyer and Finkelmann,[15] and Hanson, Dekker, and Van der Woude[16] have analyzed the pitch of a number of binary cholesteric systems that exhibit helix inversion as a function of composition, on the basis of the theory of Goossens. Although the theory allows a good mathematical fit to the experimental values, the latter authors have pointed out that the results cannot be interpreted in a physically consistent way in terms of dipole–dipole and dipole–quadrupole dispersion interactions. Such an interpretation would require certain relations to be satisfied between various parameters, and this turns out not to be the case.

In connection with our interpretation of the temperature dependence of $q$ we wish to point out that the anharmonic terms introduced in Sec. V bear some relation to the anharmonicity introduced by Keating in his twiston model. An alternative interpretation of the temperature dependence of the cholesteric wave number in dilute solutions of chiral molecules in a nematic has recently been proposed by Stegemeyer and Finkelmann.[17] In our notation they essentially start from Goossens' formula (5.3) applied to a molecular concentration $x_c$ of the chiral molecules in a nematic denoted by the subscript $n$, $q = x_c K_{nc}/2RJ_{nn}$. Here, $J_{nn}$ refers to the dipole–dipole interaction between nematogenic molecules and $K_{nc}$ to the dipole–quadrupole interaction between the nematogenic and chiral molecules. In the spirit of Goossens' theory, they consider this formula as applying to the state in which the molecules are oriented coplanar with respect to each other. In order to account for the temperature dependence of $q$ they assume hindered rotation of the molecules along their long axes and for this purpose introduce a rotational order parameter $S_R = \cos 2\psi$, where $\psi$ is the rotation angle. Assuming a potential energy $U(\psi) < k_B T$ for the hindered rotation and modifying the formula for $q$ in a somewhat *ad hoc* manner by writing $q = (x_c K_{nc}/2RJ_{nn})S_R$, Stegemeyer and Finkelmann find

$$\frac{1}{q}\frac{dq}{dT} = \frac{1}{S_R}\frac{dS_R}{dT} = -\frac{1}{T_c} \approx -0.003 .$$

Experimental data for a number of chiral molecules in nematic MBBA are indeed in rough agreement with this result. Note, however, that these arguments applied to one-component systems would predict the wrong sign because experimentally $(dq/dT)$ and $q$ have the same sign.

Finally, it should be remarked that our theory can easily be extended to binary cholesteric mixtures.

*Note added in proof*: At the Sixth International Liquid Crystal Conference (August 23–27, 1976, Kent State University) we learned that Lin-Liu and Woo have independently arrived at the conclusion that the temperature dependence of the cholesteric pitch is determined by the ratio of $\bar{P}_4$ and $\bar{P}_2$. Their results are based on an extension of a planar model discussed by Y. R. Lin-Liu, Yu Ming Shih, Chia-Wei Woo, and H. T. Tan [Phys. Rev. A **14**, 445 (1976)].

## ACKNOWLEDGMENTS

This work was performed as part of the research program of the "Stichting voor Fundamenteel Onderzoek der Materie" (F.O.M.) with financial support from the "Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek" (Z.W.O.).

## APPENDIX

Let $\mathbf{n}$ and $\mathbf{m}$ be two vectors, which are not affected by the rotation of molecule $i$. Choose a Cartesian coordinate system with unit vectors $\mathbf{x}$, $\mathbf{y}$, and $\mathbf{z}$ such that $\mathbf{a}_i = \mathbf{z}$. Then we have

$$(\mathbf{b}_i \circ \mathbf{n})(\mathbf{b}_i \cdot \mathbf{m}) = [(\mathbf{b}_i \cdot \mathbf{x})n_x + (\mathbf{b}_i \cdot \mathbf{y})n_y][(\mathbf{b}_i \circ \mathbf{x})m_x + (\mathbf{b}_i \circ \mathbf{y})m_y] = n_x m_x \cos^2\phi_i + n_y m_y \sin^2\phi_i + (n_x m_y + n_y m_x) \sin\phi_i \cos\phi_i ,$$

with $\mathbf{b}_i \cdot \mathbf{x} = \cos\phi_i$ and $\mathbf{b}_i \cdot \mathbf{y}_i = \sin\phi_i$. The assumption of uncorrelated rotations around the long molecular axes means that we are allowed to average over $\phi_i$ or

$$\overline{(\mathbf{b}_i \cdot \mathbf{n})(\mathbf{b}_i \cdot \mathbf{m})}^{\mathrm{av}} = \tfrac{1}{2}(n_x m_x + n_y m_y) = \tfrac{1}{2}(\mathbf{n} \cdot \mathbf{m}) - \tfrac{1}{2}(\mathbf{n} \cdot \mathbf{a}_i)(\mathbf{m} \circ \mathbf{a}_i) .$$

In the same way the result for

$$\overline{(\mathbf{c}_i \circ \mathbf{n})(\mathbf{c}_i \cdot \mathbf{m})}^{\mathrm{av}}$$

is obtained. Further,

$$(\mathbf{b}_i \cdot \mathbf{n})(\mathbf{c}_i \cdot \mathbf{m}) = [(\mathbf{b}_i \cdot \mathbf{x})m_x + (\mathbf{b}_i \cdot \mathbf{y})m_y][(\mathbf{c}_i \circ \mathbf{x})m_x + (\mathbf{c}_i \circ \mathbf{y})m_y] = (n_y m_y - n_x m_x)\cos\phi_i \sin\phi_i + n_x m_y \cos^2\phi_i - n_y m_x \sin^2\phi_i .$$

Averaging yields

$$\overline{(\mathbf{b}_i \circ \mathbf{n})(\mathbf{c}_i \cdot \mathbf{m})}^{\mathrm{av}} = \tfrac{1}{2}(n_x m_y - n_y m_x) = \tfrac{1}{2}\mathbf{n} \times \mathbf{m} \cdot \mathbf{a}_i .$$

As an example we consider the term

$$S = |p_{xi}^{on}|^2 |p_{yj}^{on}|^2 [(\mathbf{a}_i \circ \mathbf{c}_j) - 3(\mathbf{a}_i \cdot \mathbf{u}_{ij})(\mathbf{c}_j \cdot \mathbf{u}_{ij})]^2 ,$$

which appears in the expression for the induced dipole–dipole interaction. Averaging over molecules $i$ and $j$ gives

$$\overline{S} = |p_{xi}^{on}|^2 |p_{yj}^{on}|^2 \{\tfrac{1}{2} + \tfrac{3}{2}(\mathbf{a}_i \circ \mathbf{u}_{ij})^2 - \tfrac{1}{2}[(\mathbf{a}_i \circ \mathbf{a}_j) - 3(\mathbf{a}_i \cdot \mathbf{u}_{ij})(\mathbf{a}_j \circ \mathbf{u}_{ij})]^2\} .$$


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